

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Serial No. : 10/532,832

Filed : January 4, 2006

For :COSMETIC EXCELLENT IN TEXTURE AND
OIL-DISPERSIBILITY

Art Unit & Examiner : 1616, FISHER ABIGAIL L.

DECLARATION UNDER 37 C.F.R. 1.132

Honorable Commissioner of Patents and Trademarks
ALEXANDRIA, VIRGINIA 22313

Sir:

I, the undersigned Hideki Nakata do hereby declare

That I completed the master course in the graduate school of science in Hokkaido University in March 2007 , entered Idemitsu Kosan Co., Ltd. in April 2007, and since 2007 , have occupied in a research and development in the field of particle technology up to now;

That I am a co-worker with the inventor of the present invention;

That I have a good knowledge of the English language and have read and understood the application papers and the Examiner's Official Action as well as the reference cited therein in the prosecution of the above identified patent application; and

That, in order to show the different between the subject matter of reference (JP09-202825) and the subject matter of the application, the following experiment was carried out.

Water Absorption was examined about poly- γ -glutamic acid and polyaspartic acid according to JP9-202825A. JP9-202825A discloses production of crosslinked material of polyaspartic acid having an absorption ability of 200 times as much as the weight of the crosslinked material by a tea bag method. According to the examples 1 and 8 of JP9-202825A, the results are shown in the Table-A below.

Measurement of water ability

A 10% by weight aqueous solution of poly- γ -glutamic acid (Caltake (trade name) available from Ajinomoto Co., Inc. , Molecular Weight; 70000 - 80000) was irradiated with electron beam at an intensity 140, 120, 100 and 80 kGy, respectively. The resultant treated material was immersed in water at 4°C for one week to remove uncrosslinked poly- γ -glutamic acid therefrom. The water-swelled poly- γ -glutamic acid gel was separated by filtration through a metal screen with 80 mesh and was weighed (W1;wet weight). The water-swelled poly- γ -glutamic acid gel was dried and weighed (W2;dry weight). The absorption ability was calculated by the equation, Water Ability = $(W1 - W2)/W2$. The results are shown in the Table-A below.

Table-A

Electron Beam Irradiation(kGy)	Absorption Ability (Times)	
	poly- γ -glutamic acid	asparatic acid
140	347.17	—
120	563.35	—
100	975.22	25
80	2658.79	460

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Hideki Nakata

Hideki Nakata

Date; FEB. 19. 2009

Exhibit A

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-202825

(43) 公開日 平成9年(1997)8月5日

(51) Int.Cl. ⁸	識別記号	庁内整理番号	P I	技術表示箇所
C 0 8 G 69/48	NRH		C 0 8 G 69/48	NRH
73/10	NTE		73/10	NTE
C 0 8 J 3/28	CEZ		C 0 8 J 3/28	CEZ

審査請求 未請求 請求項の数 2 O L (全 7 頁)

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(54) 【発明の名称】 ポリアスバラギン酸架橋体の製造方法

(57) 【要約】

【課題】 ポリアスバラギン酸の架橋体の製造方法を提供する。

【解決手段】 ポリアスバラギン酸を溶媒に溶解して得られる溶液に放射線を照射して該架橋体を得る。

(2)

特開平9-202825

1

【特許請求の範囲】

【請求項1】 ポリアスバラギン酸を溶媒に溶解して得られる溶液に放射線を照射してポリアスバラギン酸架橋体を得ることを特徴とするポリアスバラギン酸架橋体の製造方法。

【請求項2】 ティーバッグ法によるポリアスバラギン酸架橋体の吸水能が架橋体重量に対して200重量倍以上である請求項1記載のポリアスバラギン酸架橋体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、新規なポリアスバラギン酸架橋体の製造方法に関する。詳しくは、生分解性を有し、増粘剤や吸水性樹脂として利用可能な、ポリアスバラギン酸から誘導される架橋体及びその製造方法に関するものである。本発明により得られるポリアスバラギン酸架橋体は、生分解性を有し、その用途は多岐にわたり特に限定的でなく、例としては、各種高分子エマルジョン、ラテックス等の増粘剤、止水材、土壌改良剤、園芸用保水剤、あるいは紙おむつ、生理用品等の使い捨ての衛材、表面処理剤、シール剤等に利用しう。

【0002】

【従来の技術】 吸水性樹脂としては従来、ポリビニルアルコール、ポリエチレンオキシド、ポリアクリル酸ソーダ等が知られている。また、架橋体としても、カルボキシメチルセルロース架橋体、ポリエチレンオキシド部分架橋体、デンプン-アクリロニトリルグラフト共重合体の加水分解物、ビニルアルコール-アクリル酸塩共重合体等がある。

【0003】 しかしながら、これらの樹脂は、いずれも十分な性能を有するものではなく、生分解性あるいは加水分解性が低く、使用後廃棄あるいは放置されると自然環境中に残存し、周辺環境に悪影響を与えかねないものであるか、生分解性が高くとも吸水性や加圧保水力が低いものであった。このため、近年、生分解性あるいは加水分解性を有するポリアミノ酸から高吸水性架橋体を得るための研究が行われており、例えば、ポリアスバラギン酸やポリグルタミン酸等の酸性アミノ酸系樹脂の側鎖をエステル化した樹脂をジアミンで架橋した後、エステル残基をカルボキシル化あるいはその塩に変換することにより吸水性樹脂を生成する技術（特公昭52-41309号公報）、ポリコはく酸イミドをジアミンで架橋した後、加水分解することによりポリアスバラギン酸系の吸水性樹脂を生成する技術（特開平7-224163号公報）などが開示されている。

【0004】 しかしながら、これらの製法は工業的には複雑な操作を必要とし、原材料費も高く、コスト的に問題がある。一方、ポリ（γ-グルタミン酸）溶液にγ線を照射すること（高分子論文集、第50巻10号、755頁（1993））及びポリ（γ-リジン）にγ線をす

2

ること（繊維学会誌、第51巻3号、137頁（1995））により生分解性高吸収体を製造する技術が報告されている。

【0005】 しかしながら、上記の方法は、その原料において高価なアミノ酸を用いる必要があり、更に、そのポリマーを得るためには、微生物を使用したり、モノマーのN-カルボキシ無水物を使用する等、高価な方法を用いる必要がある。

【0006】

10 【発明が解決しようとする課題】 本発明は、上記問題を解決すべく、生分解性を有するポリアミノ酸類であるポリアスバラギン酸から簡便かつ安価に高吸水性架橋体を提供することを目的とする。

【0007】

【課題を解決するための手段】 本発明者らは、上記課題を解決すべく鋭意検討した結果、ポリアスバラギン酸溶液に放射線を照射することにより、簡便かつ安価に新規なポリアスバラギン酸架橋体を得られることを見出し、本発明を解決するに至った。すなわち、本発明の要旨は、ポリアスバラギン酸を溶媒に溶解して得られる溶液に放射線を照射してポリアスバラギン酸架橋体を得ることを特徴とするポリアスバラギン酸架橋体の製造方法に存する。

【0008】

【発明の実施の形態】 以下、本発明についてさらに詳細に説明する。本発明に使用されるポリアスバラギン酸の製造法は特に限定的ではないが、例えば、アスバラギン酸をリン酸存在下、または無触媒下で加熱し、脱水縮合させることによりポリコはく酸イミドを得ることができる（特公昭48-20638号公報等）。また、ポリコはく酸イミドを加水分解してポリアスバラギン酸を得る反応は公知であり、これによりポリアスバラギン酸を製造することができる。

【0009】 ポリコはく酸イミドの重量平均分子量は、熱縮合の温度、触媒の種類（リン酸、ポリリン酸または他の脱水剤）や添加量、反応系内の圧力（減圧度）等によって変わるが、一般に重量平均分子量1,000以上であれば良いが、水不溶性の架橋体を得るためには高分子量体が有利であり、好ましくは10,000以上、より好ましくは20,000以上、最も好ましくは30000以上である。

【0010】 本発明に使用されるポリアスバラギン酸の中和度には特に制限はないが、中和度（すべてカルボン酸である状態が中和度0である。）が低すぎると吸水能の低下を招き、あるいは放射線照射中の分解反応が進行しやすくなるため、好ましくは20~100%、より好ましくは30~100%であり、最も好ましくは50~100%で有り、ポリコはく酸イミドの加水分解後、もし必要であれば塩酸、硫酸等の鉱酸類、蟻酸、酢酸等の有機酸類、特に好ましくは安価で取り扱いの容易な塩酸

50

(3)

特開平9-202825

3

4

を用いて所望の中和度のポリアスパラギン酸溶液を得ることができる。

【0011】本発明において、ポリアスパラギン酸を混合、溶解させる溶媒は通常水であるが、水と水溶性液体の混合物を用いることもできる。ここでいう水溶性液体に特に制限はないが、例としては、メチルアルコール、エチルアルコール、イソプロパノール等のアルコール類、アセトン、メチルエチルケトン、メチルイソブチルケトン等のケトン類、酢酸メチル、酢酸エチル等のエステル類等が挙げられる。また、水と水溶性液体との混合比は用いる水溶性液体により異なるが、ポリアスパラギン酸を溶解させよう、水を主成分とし、水溶性溶媒の量は適宜調整するのがよい。

【0012】上記溶液におけるポリアスパラギン酸の濃度は、好ましくは0.1~50重量%であり、より好ましくは1~25重量%である。本発明におけるポリアスパラギン酸を溶媒に混合、溶解して得られる溶液に放射線を照射する際に用いる容器としては放射線透過性の容器であれば特に制限はなく、ガラス製の密閉可能な瓶等が好ましく挙げられる。

【0013】本発明に使用される放射線として、好ましくは α 線、 β 線、 γ 線、電子線、中性子線、X線、荷電粒子線が挙げられ、より好ましくは γ 線が用いられる。また、目的物をフィルムあるいはシート状で製造する場合は、透過力の小さい α 線、 β 線、電子線を用いるのが好ましい。該放射線に γ 線を使用する場合、 γ 線吸収量は好ましくは1~500kGy、より好ましくは5~500kGyであり、最も好ましくは、10~500kGyであり、通常室温、常圧下で架橋が進行する。また、系内の雰囲気については空気存在下でも架橋は進行するが、架橋度が上がりにくくなるため、窒素、アルゴン等の不活性ガス中であるのが、より好ましい。

【0014】該 γ 線については特に限定的ではないが、例えばコバルト60を線源とする照射装置等により発生させたものを用いることができる。本発明における架橋体の吸水能は、ティーバック法により求めた。本発明においてティーバック法とは、ビーカーに蒸留水を入れ、ナイロンネット(NBC工業(株)社製、N-255HD、250mesh)で作った袋(深さ20cm×幅10cm)に試料を入れて浸し、冷暗所で一昼夜静置した後、袋ごと取り出し、室温にて15分間吊して水切りしたものを計量する手法をいう。即ち、吸水量は最終重量から架橋体重量及び袋重量を差し引いた値を架橋体重量で割った値となる。吸水量について、特に制限はないが、吸水性樹脂としての実用性を考えると、好ましくは、200重量倍以上、更に好ましくは、300重量倍以上、最も好ましくは、500重量倍以上である。

【0015】このようにして得られたポリアスパラギン酸架橋体粗製物は、通常、無色透明なゲルであり、そのまま吸水性材料として用いることができるが、必要であ

れば浸せき、透析、あるいは再沈殿、濾過、洗浄、乾燥等通常の方法により精製することができる。得られたポリアスパラギン酸架橋体は、水不溶性且つ吸水性を有する白色、あるいは黄色の固体であり、通常、有機溶媒に膨潤、または不溶で、加熱しても溶解しない。

【0016】以下、実施例によって本発明をより具体的に説明するが、本発明はこれらの実施例に限定されるものではない。

【0017】

【実施例】本発明に使用されたポリアスパラギン酸の分析は下記の測定方法で行った。

1) 重量平均分子量

ポリこはく酸イミドの重量平均分子量は、東ソー(株)社製「TSK gel」"GMHHR-M" + 「TSK gel」"G2000HHR" カラム、および溶離液として10mM臭化リチウムのジメチルホルムアミド溶液を用いたゲルパーミエーションクロマトグラフ(示差屈折計)により得られたポリスチレン換算値である。

【0018】ポリアスパラギン酸の重量平均分子量は、東ソー(株)社製「TSK gel」"G6000PWL" + 「TSK gel」"G3000PWL" カラム、および溶離液として0.4M硝酸ナトリウム水溶液を用いたゲルパーミエーションクロマトグラフ(示差屈折計)により得られたポリエチレングリコール換算値である。

【0019】2) 吸水能

放射線照射により得られたゲルを蒸留水に浸せきすることにより未架橋の高分子や分解生成物等の水溶性物質を除去した後、濾別、乾燥して架橋体を得た。これら各架橋体の粒子(30~180mesh)0.1gを用いて、ティーバック法により、吸水能を求めた。

【0020】具体的には、400mlの蒸留水の入った500mlビーカーに、ナイロンネット(NBC工業(株)社製、N-255HD、250mesh)で作った袋(深さ20cm×幅10cm)に上記試料を入れて浸し、冷暗所で一昼夜静置した後、袋ごと取り出し、室温にて15分間吊して水切りしたものを計量した。該重量から架橋体重量(0.1g)及び袋重量を差し引いた値を架橋体重量(0.1g)で割った値を吸水量(g-水/g-ポリマー)として求めた。

【0021】【参考例1】ポリこはく酸イミド(分子量100,000)の合成

2Lのナス型フラスコにL-アスパラギン酸100gおよびリン酸50gを仕込み、180℃、減圧度約5mmHgの条件下で、ロータリーエバポレーターを使用して回転させながら3.5時間反応させた後、ナス型フラスコ中にジメチルホルムアミド400mlを加え、120℃で生成物を均一溶解させた。この溶液を純水1.5Lに滴下し得られたスラリーをミキサーで粉砕した後、減圧濾過した。これを純水で濾液が中性になるまで懸洗

(4)

特開平9-202825

5

6

し、得られたケーキを150℃で24時間熱風乾燥し、白色粉末を得た。このポリコはく酸イミドの重量平均分子量は100,000、ポリマーへの転化率は97.8%であった。

【0022】【参考例2】ポリコはく酸イミド(分子量70,000)の合成

冷却器、温度計、攪拌器および水分離器を備えた200mlの四つ口フラスコ内に、アスパラギン酸25g、85%リン酸2.5g、メシチレン56gおよびスルホラン24gを仕込んだ。次いで、常圧、メシチレンの還流下(162℃)に4.5時間保ち、重合を行った。反応中に生じた水はメシチレンの一部と共に系外へ留去せしめた。反応終了後、濾別し、生成物を純水100gで4回、メタノール100gで1回洗浄した。次いで、これを減圧下80℃で24時間乾燥し、黄白色の粉末を得た。このポリコはく酸イミドの重量平均分子量は70,000、ポリマーへの転化率は98%であった。

【0023】【参考例3】ポリコはく酸イミド(分子量40,000)の合成

シクロヘキシルアミン0.92gをアスパラギン酸等と

一緒に加えた以外、参考例2と同様に行った。このポリコはく酸イミドの重量平均分子量は40,000、ポリマーへの転化率は95%であった。

【参考例4】ポリコはく酸イミド(分子量24,000)の合成

リン酸を2.5gから0.18gにした以外、参考例2と同様に行った。このポリコはく酸イミドの重量平均分子量は24,000、ポリマーへの転化率は59%であった。

【0024】【参考例5】ポリアスパラギン酸の合成
参考例1, 2, 3, 4または5で得られたポリコはく酸イミドを水に懸濁させた液に等モル量のNaOH水溶液を滴下し、加水分解を完了させた後、必要な場合は1N塩酸水溶液にて中和度を調整した。得られたポリアスパラギン酸水溶液を大量のメタノールに滴下し、これを加圧濾過、洗浄、乾燥し、ポリアスパラギン酸を得た。この結果を表1に示した。

【0025】

【表1】

ポリコはく酸イミド 重量平均分子量	ポリアスパラギン酸重量平均分子量	
	70%	100%
24,000	25,000	25,000
40,000	52,000	53,000
70,000	90,000	87,000
100,000	120,000	120,000

【実施例1〜37】参考例6で得たポリアスパラギン酸を用い、分子量、中和度等を変化させた場合の架橋体の生成条件および吸水能変化を検討した。即ち、該ポリアスパラギン酸の1〜50%水溶液を調整し、それぞれ5ml用ガラス製サンプル瓶に2mlずつ分注した後、密閉し、20℃にてγ線を照射した。尚、コバルト60

(110TBq)を線源として備えたγ線照射装置(三菱重工業(株)社製)を用い、γ線を照射した。この結果を表2に示した。

【0026】

【表2】

(5)

特開平9-202825

7

8

表 2

実施例	γ 重量[%]	重量平均分子量	中和度[%]	除酸精度[%]	吸水倍
1	100	25.000	70	10	25
2				25	45
3				50	70
4			100	10	20
5				25	40
6				50	65
7	80	52.000	70	5	510
8				10	400
9				25	310
10				50	130

【0027】

【表3】

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(6)

特開平9-202825

9

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表 2 の つ い て

実施例	r 値(%)	重量平均分子量	中和度(%)	粘度(%)	吸水率
11	80	53.000	100	5	270
12				10	730
13				25	500
14				50	150
17	60	90.000	70	1	600
18				5	1,100
19				10	3,400
20				25	2,300
22	60	87.000	100	1	700
23				5	3,200
24				10	1,000
25				25	190

【0028】

30 【表4】

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特開平9-202825

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表 2 の つ つ 6

実施例	r 単位(%)	重量平均分子量	中和度(%)	市販量(%)	親水性
26	40	120,000	70	1	2,800
27				5	3,100
28				10	950
29			100	1	2,400
30				5	3,000
31				10	1,300
32	31	80,000	70	1	240
33				5	120
34		87,000	100	1	32
35	20	120,000	70	1	300
36				5	150
37			100	1	80

【0029】

【発明の効果】 本発明によれば、高い生分解性を有し、増粘剤や吸水性樹脂等として利用可能な、各種の工

30 業的応用が期待される安価且つ新規なポリスバラギン酸架橋体が得られる。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-202825

(43)Date of publication of application : 05.08.1997

(51)Int.Cl.

C08G 69/48
C08G 73/10
C08J 3/28

(21)Application number : 08-011691

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(22)Date of filing : 26.01.1996

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(54) PRODUCTION OF CROSSLINKED MATERIAL OF POLYASPARTIC ACID

(57)Abstract:

PROBLEM TO BE SOLVED: To simply and inexpensively obtain the subject new crosslinked material usable as a thickening agent, a water-absorbing resin, etc., high in biodegradability, by irradiating a solution of a polyaspartic acid with radiation.

SOLUTION: A polyaspartic acid is dissolved in a solvent and the prepared solution is irradiated with radiation to give the objective crosslinked material having an absorption ability of 200 times as much as the weight of the crosslinked material by a tea bag method. For example, the neutralization degree of the polyaspartic acid is 50-100%, and a mixture of water as a main component with a water-soluble liquid such as methyl alcohol is used as the solvent. The radiation is γ -rays and the γ -ray absorbed dose is preferably 10-500kGy.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of a new polyaspartic acid bridging body. In detail, it has biodegradability and is related with a bridging body available as a thickener or hydrophilic resin derived from polyaspartic acid, and a manufacturing method for the same. The polyaspartic acid bridging body obtained by this invention, It has biodegradability, and it is especially various, and the use is not restrictive, and can be used for the ** material of throwing away of thickeners, such as various polymer emulsions and latex, a stop material, a soil conditioner, the water retention agent for horticulture or a disposable diaper, sanitary items, etc., a finishing agent, a sealing compound, etc. as an example,

[0002]

[Description of the Prior Art]As hydrophilic resin, polyvinyl alcohol, polyethylene oxide, sodium polyacrylate, etc. are known conventionally. There are hydrolyzate of a carboxymethyl cellulose bridging body, a polyethylene oxide partial bridging body, and a starch acrylonitrile graft copolymer, a vinyl alcohol acrylate copolymer, etc. also as a bridging body.

[0003]However, no these resin is what has sufficient performance, Biodegradability or hydrolysis nature was low, when discarded or neglected after use, it remained in natural environment, and it may have an adverse effect on peripheral environment, and absorptivity and application-of-pressure water holding capacity were low in biodegradability being high. For this reason, research for obtaining a high absorptivity bridging body from the polyamino acid which has biodegradability or hydrolysis nature in recent years is done, For example, after constructing a bridge by diamine in the resin which esterified the side chain of acidic-amino-acid system resin, such as polyaspartic acid and polyglutamic acid, The art which generates hydrophilic resin by changing ester residue into carboxylation or its salt (JP,52-41309,B), The art (JP,7-224163,A) etc. which generate the hydrophilic resin of a polyaspartic acid system are indicated by hydrolyzing poly amide acid imide, after constructing a bridge by diamine.

[0004]However, these processes need complicated operation industrially, and a material cost is also high and has a problem in cost. On the other hand, The art of manufacturing a biodegradable quantity absorber is reported by by making a gamma ray irradiating a poly (gamma-glutamic acid) solution with a gamma ray (polymers collected papers, volume [50th] No. 10, 755 pages (1993)), and poly (epsilon-lysine) (the Society of Fiber Science and Technology, Japan, volume [51st] No. 3, 137 pages (1995)).

[0005]However, expensive amino acid needs to be used for the above-mentioned method in the raw material, and further, in order to obtain the polymer, expensive methods, such as using a microorganism or using N-carboxyanhydride of a monomer, need to be used for it.

[0006]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide a high absorptivity bridging body simple and cheaply from the polyaspartic acid which is polyamino acid which has biodegradability that the above-mentioned problem should be solved.

[0007]

[Means for Solving the Problem]This invention persons came to solve an obtaining [a simple and

cheaply new polyaspartic acid bridging body] title and this invention by irradiating a polyaspartic acid solution with radiation, as a result of inquiring wholeheartedly that an aforementioned problem should be solved. That is, a gist of this invention consists in a manufacturing method of a polyaspartic acid bridging body irradiating with radiation a solution produced by dissolving polyaspartic acid in a solvent, and obtaining a polyaspartic acid bridging body.

[0008]

[Embodiment of the Invention] Hereafter, it explains still in detail about this invention. Although the manufacturing method in particular of the polyaspartic acid used for this invention is not restrictive, poly amber acid imide can be obtained by heating and carrying out dehydration condensation of the aspartic acid under phosphoric acid existence or a non-catalyst, for example (JP,48-20638,B etc.). The reaction which hydrolyzes poly amber acid imide and obtains polyaspartic acid is publicly known, and, thereby, can manufacture polyaspartic acid.

[0009] Although the weight average molecular weight of poly amber acid imide changes with the temperature of heat condensation, the kind (phosphoric acid, polyphosphoric acid, or other dehydrators) of catalyst, the pressure (decompression degree) within an addition and the system of reaction, etc., Although what is necessary is generally just 1,000 or more weight average molecular weight, it is 30000 or more most preferably 20,000 or more 10,000 or more preferably [in order to obtain the bridging body of insoluble in water nature, the amount object of polymers is advantageous, and].

[0010] Although there is no restriction in particular in the degree of neutralization of the polyaspartic acid used for this invention, Since the fall of water absorption power will be caused or the decomposition reaction under radiation irradiation will advance easily, if the degree of neutralization (the state of being carboxylic acid altogether is the degree 0 of neutralization.) is too low, It is 30 to 100% more preferably 20 to 100%, It is at 50 to 100% most preferably, and after hydrolysis of poly amber acid imide, if required, the polyaspartic acid solution of the desired degree of neutralization can be obtained using organic acid, such as mineral acid, such as chloride and sulfuric acid, formic acid, and acetic acid, and the chloride of handling cheap especially preferably and easy.

[0011] In this invention, although the solvent in which polyaspartic acid is mixed and dissolved is the indifferent water, the mixture of water and a water-soluble fluid can also be used. Although there is no restriction in particular in a water-soluble fluid here, as an example, ester species, such as ketone, such as alcohols, such as methyl alcohol, ethyl alcohol, and isopropanol, acetone, methyl ethyl ketone, and methyl isobutyl ketone, methyl acetate, and ethyl acetate, etc. are mentioned. Although the mixture ratio of water and a water-soluble fluid changes with water-soluble fluids to be used, water is used as the main ingredients and the quantity of a water-soluble solvent is good to adjust suitably so that it may be made to dissolve and may deal in polyaspartic acid.

[0012] The concentration of the polyaspartic acid in the above-mentioned solution is 0.1 to 50 % of the weight preferably, and is 1 to 25 % of the weight more preferably. If it is a radiolucent container as a container used when irradiating with radiation the solution produced by mixing and dissolving the polyaspartic acid in this invention in a solvent, there will be no restriction in particular and the bottle etc. in which glass sealing is possible will be mentioned preferably.

[0013] As radiation used for this invention, alpha rays, a beta ray, a gamma ray, an electron beam, a neutron beam, X-rays, and a charged particle beam are mentioned preferably, and a gamma ray is used more preferably. When manufacturing an object by the film or a sheet shaped, it is preferred to use the small alpha rays of penetrating power, a beta ray, and an electron beam. When using a gamma ray for this radiation, a gamma ray absorbed amount is 5 - 500kGy more preferably one to 500 kGy, most preferably, it is 10 - 500kGy and bridge construction usually advances under a room temperature and ordinary pressure. Although bridge construction advances also under air existence about the atmosphere in a system, since it becomes difficult to go up a degree of cross linking, it is more preferred that it is among inactive gas, such as nitrogen and argon.

[0014] Although it is not restrictive about this gamma ray in particular, the thing which made it generate with the irradiation equipment etc. which make 60Co a line source, for example can be

used. It asked for the water absorption power of the bridging body in this invention by the tea bag method. putting distilled water into a beaker with the tea bag method in this invention — a nylon net (NBC Industrial company make.) After putting in and dipping a sample in the bag (depth [of 20 cm] x10 cm in width) made from N-255HD and 250mesh and settling in a cool place one whole day and night, the whole bag is taken out and the technique of measuring that which was hung for 15 minutes and from which it drained off water at the room temperature is said. That is, a coefficient of water absorption serves as a value which broke by bridging body weight the value which deducted bridging body weight and bag weight from the final mass. Although there is [coefficient of water absorption] no restriction in particular, when the practicality as hydrophilic resin is considered, it is [more than 200 weight double] more than 500 weight twice most preferably more than 300 weight double still more preferably.

[0015] Thus, although it is water-white gel and can usually use as an absorptivity material as it is, if the obtained polyaspartic acid bridging body crude things are required, they can be refined by the usual methods, such as a dipping, dialysis or reprecipitation, filtration, washing, and desiccation. the obtained polyaspartic acid bridging body is a white or yellow solid which has insoluble in water nature and absorptivity — usually — an organic solvent — swelling — or even if it is insoluble and heats, it does not fuse.

[0016] Hereafter, although an example explains this invention more concretely, this invention is not limited to these examples.

[0017]

[Example] Analysis of the polyaspartic acid used for this invention was conducted by the following measuring method.

1) The weight average molecular weight of weight-average-molecular-weight poly amber acid imide, The "TSKgel" "GMHHR-M" + "TSKgel" "G2000HHR" column by TOSOH [CORP.] CORP., And it is the polystyrene reduced property obtained by the gel permeation chromatograph (differential refractometer) using the dimethylformamide solution of 10mM lithium bromide as an eluate.

[0018] The weight average molecular weight of polyaspartic acid The "TSKgel" "G6000PWXL" + "TSKgel" "G3000PWXL" column by TOSOH [CORP.] CORP., And it is the polyethylene-glycol reduced property obtained by the gel permeation chromatograph (differential refractometer) using 0.4M sodium nitrate solution as an eluate.

[0019] 2) After removing water soluble matter, such as polymers unconstructed a bridge and a decomposition product, by carrying out the dipping of the gel obtained by water-absorption-power radiation irradiation to distilled water, it dried and the ** exception obtained the bridging body. It asked for water absorption power by the tea bag method using 0.1 g of particles (30 - 180mesh) of these each bridging body.

[0020] the 500-ml beaker into which 400 ml of distilled water specifically went — a nylon net (NBC Industrial company make.) After putting in and dipping the above-mentioned sample in the bag (depth [of 20 cm] x10 cm in width) made from N-255HD and 250mesh and settling in a cool place one whole day and night, the whole bag was taken out and that which was hung for 15 minutes and from which it drained off water at the room temperature was measured. The value which broke by bridging body weight (0.1g) the value which deducted bridging body weight (0.1g) and bag weight from this weight was calculated as a coefficient of water absorption (g-water / g-polymer).

[0021] [Reference example 1] Teach 100g of L-aspartic acid, and the phosphoric acid 50g to the eggplant type flask of the composition 2L of poly amber acid imide (molecular weight 100,000), and under 180 ** and the conditions of the about 5 decompression degree mmHg(s). After making it react for 3.5 hours, making it rotate using a rotating evaporator, 400 ml of dimethylformamide was added into the eggplant type flask, and the uniform dissolution of the output was carried out at 120 **. After the mixer ground the slurry which might be dropped at the pure water 1.5L in this solution, filtration under reduced pressure was carried out. This was ****(ed) until filtrate became neutrality with pure water, hot air drying of the obtained cake was carried out at 150 ** for 24 hours, and white powder was obtained. The inversion rate to 100,000 and polymer of the weight average molecular weight of this poly amber acid imide was 97.8%.

[0022][Reference example 2] 25 g of aspartic acid, the 85% phosphoric acid 2.5g, 56g of mesitylene, and 24 g of sulfolane were taught in the 200-ml 4 mouth flask provided with the synthetic condensator, the thermometer, stirrer, and mist separator of poly amber acid imide (molecular weight 70,000). Subsequently, it maintained under flowing back of ordinary pressure and mesitylene (162 **) for 4.5 hours, and the polycondensation was performed. The water produced during the reaction was made to distill off out of a system with a part of mesitylene. After ending reaction and a ** exception carried out, and the pure water 100g washed output once with the methanol 100g 4 times. Subsequently, this was dried at 80 ** under decompression for 24 hours, and the powder of yellowish white was obtained. The inversion rate to 70,000 and polymer of the weight average molecular weight of this poly amber acid imide was 98%.

[0023][Reference example 3] It carried out like the reference example 2 except having added 0.92 g of synthetic cyclohexylamine of poly amber acid imide (molecular weight 40,000) together with aspartic acid etc. The inversion rate to 40,000 and polymer of the weight average molecular weight of this poly amber acid imide was 95%.

[Reference example 4] It carried out like the reference example 2 except synthetic phosphoric acid of poly amber acid imide (molecular weight 24,000) having been 0.18 g from 2.5g. The inversion rate to 24,000 and polymer of the weight average molecular weight of this poly amber acid imide was 59%.

[0024][Reference example 5] After dropping the NaOH aqueous solution of the equimolecular amount at the liquid which made the poly amber acid imide obtained by the synthetic reference example 1, 2, 3, 4, or 5 of polyaspartic acid suspended in water and making hydrolysis complete, when required, the degree of neutralization was adjusted with 1N hydrochloric acid aqueous solution. The obtained polyaspartic acid solution was dropped at a lot of methanol, and this was filtered under pressure, and it washed, and dried, and polyaspartic acid was obtained. This result was shown in Table 1.

[0025]

[Table 1]

ポリコハク酸イミド 置換平均分子量	ポリアスパラギン酸置換平均分子量	
	70%	100%
24,000	25,000	25,000
40,000	52,000	53,000
70,000	90,000	87,000
100,000	120,000	120,000

[Examples 1-37] The generation condition of the bridging body at the time of changing a molecular weight, the degree of neutralization, etc. and water-absorption-power change were considered using the polyaspartic acid obtained by the reference example 6. That is, after adjusting the 1 to 50% solution of this polyaspartic acid and pouring 2 ml distributively to each glass sample bottles for 5 ml, respectively, it sealed and irradiated with the gamma ray at 20 **. It irradiated with the gamma ray using the gamma irradiation device (made by Mitsubishi Heavy Industries, LTD., LTD.) provided with 60Co (110TBq) as a line source. This result was shown in Table 2.

[0026]

[Table 2]

表 2

実施例	r 値 (kg)	重量平均分子量	中和度 (%)	膨張率 (%)	吸水率
1				10	25
2	100	25,000	70	25	45
3				50	70
4			100	10	20
5				25	40
6				50	85
7				5	510
8	80	52,000	70	10	480
9				25	510
10				50	130

[0027]

[Table 3]

表 2 の つ い き

実施例	γ 射线 (467)	重量平均分子量	中和度 (%)	粘度 (dl/g)	吸水率
11	80	53,000	100	5	270
12				10	730
13				25	500
14				50	150
17	63	90,000	70	1	600
18				5	1,100
19				10	3,400
20				25	2,300
22		87,000	100	1	700
23				5	3,200
24				10	1,000
25				25	190

[0028]
[Table 4]

表 2 の つ づ き

実施例	r 値 (%)	重量平均分子量	中和度 (%)	溶解濃度 (%)	吸水倍
26	40	120,000	70	1	2,800
27				5	3,100
28				10	950
29			100	1	2,400
30				5	3,000
31				10	1,300
32	31	90,000	70	1	240
33		87,000	100	5	120
34				1	32
35	20	120,000	70	1	380
36				5	150
37			100	1	86

[0029]

[Effect of the Invention] According to this invention, it has high biodegradability and the cheap and new polyaspartic acid bridging body it is expected that various kinds of industrial application available as a thickener, hydrophilic resin, etc. is obtained.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]A manufacturing method of a polyaspartic acid bridging body irradiating with radiation a solution produced by dissolving polyaspartic acid in a solvent, and obtaining a polyaspartic acid bridging body.

[Claim 2]A manufacturing method of the polyaspartic acid bridging body according to claim 1 whose water absorption power of a polyaspartic acid bridging body by the tea bag method is more than 200 weight twice to bridging body weight.

[Translation done.]